PASSIVATION POLYMER BULKING VERSUS SUCROSE IMPREGNATION: A CROSS-METHODOLOGICAL APPROACH TO THE CONSERVATION OF LEATHER

A Senior Scholars Thesis

by

LAURA GAIL WHITE

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2008

Major: Marine Sciences, Maritime Studies

PASSIVATION POLYMER BULKING VERSUS SUCROSE IMPREGNATION: A CROSS-METHODOLOGICAL APPROACH TO THE CONSERVATION OF LEATHER

A Senior Scholars Thesis

by

LAURA GAIL WHITE

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

Approved by:

Research Advisor: C. Wayne Smith
Associate Dean for Undergraduate Research: Robert C. Webb

April 2008

Major: Marine Sciences, Maritime Studies

ABSTRACT

Passivation Polymer Bulking Versus Sucrose Impregnation:

A Cross-Methodological Approach to the Conservation of Leather (April 2008)

Laura Gail White
Department of Maritime Studies
Texas A&M University

Research Advisor: Dr. C. Wayne Smith
Department of Anthropology

Archaeological leather, especially that which comes from wet excavation sites, has long challenged conservators who wish to preserve it so that it will be long lasting, stable, and informative for cultural analysis. Both the unique structure of the artifact and the detrimental waterlogged environment must be overcome to achieve acceptable results. Many methods have been used to conserve leather with varying degrees of success. The three most common methods of conservation are drying, consolidation, and the use of chemical dressings. The purpose of this research is to compare two methods of consolidation: silicone impregnation and sucrose bulking. Silicone impregnation has been used in leather conservation with excellent results, and its effects have been compared with those of several other consolidation methods, but never to sucrose. In fact, sucrose has never been used as a conservation agent in leather, and has rather been used only in the conservation of waterlogged wood. Parallel testing of polymer bulking and sucrose impregnation confirmed the superiority of samples treated with Passivation

Polymer technology in terms of retaining diagnostic characteristics. However, it also proved that sucrose impregnation may serve as a quick, cheap, and reversible method of conservation, particularly for developing conservation programs.

DEDICATION

This work is dedicated to my lab instructors, past and present: Kim Adams, Kathleen Huckabee, Susan Knock, and Grace Townsend, who taught me the value of constructive play in a lab coat and goggles.

ACKNOWLEDGMENTS

I owe a tremendous debt of gratitude to my advisor, Wayne Smith, and his wife, Helen DeWolf. They went out of their way to make me welcome in their labs and provide me with whatever I needed, be it monetary support, springboards for thought, or simply chances to get my hands dirty. Also, special thanks to Michael Pendleton and the Microscopy and Imaging Center at TAMU, who graciously allowed the use of their equipment for finicky samples. Finally, thanks to graduate students Catherine Sinchich and Eloise Eilert who offered support, feedback, and laughter on those days when everything went wrong.

NOMENCLATURE

APRL	Archaeological Preservation Research Lab
CRL	Conservation Research Lab
DBTDA	A moderate catalyst: Dibutyl Tin Diacetate
EDS	Electron-Dispersive X-ray spectroscopy
MTMS	Methyl Trimethoxysilane
PA oil	A low viscosity silicone oil
PEG	Polyethylene Glycol
Q1 oil	A medium viscosity silicone oil
SEM	Scanning Electron Microscope
TPT-titanate	A slightly more stringent catalyst than DBTDA
v/v	Volume to volume ratio
w/v	Weight to volume ratio
w/w	weight to weight ratio

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

CHAPTER I

INTRODUCTION TO THE NATURE OF LEATHER AND LEATHER CONSERVATION

The rise of nautical archaeology in the sixties and seventies required the science of archaeological conservation to come of age extremely rapidly. Waterlogged artifacts are chemically altered from their original states and are thus unstable, requiring special treatment strategies. While this is most true and most studied in the case of wooden artifacts, it is also evident in any material that has existed underwater for any length of time, save for the most impervious and noble of metals. This means that not only woods, but also textiles, paper, and animal products such as bone, leather, and ivory suffer similar sorts of degradation in wet environments due to microbial attack and the physical action of water and sediment in submerged sites. The excellent solvent properties of water lead it to naturally hydrolyze artifacts, and in the marine environment, any number of chemical inclusions may destroy an artifact's structural integrity if they are included in its cellular matrix. Artifacts can be encrusted or covered in dirt, silt, or clay and therefore difficult to clean and conserve (Cameron 2006). Sea salts are included through passive transport, and if these salts are allowed to dry, they will cause massive damage as the rapid formation of their crystalline structure will force apart the fibers or cells of an artifact. In the event that leather is found on a wet

---

This thesis follows the style of *Journal of the Society for Historical Archaeology*.

archaeological site, it is important that it is conserved properly and completely, because it is rare and can be very important for interpretation of a site.

What is leather?

Often, materials scientists and conservators are balked by the fact that there is an infinite variety of materials that may fall under a single heading, such as wood, which represents tens of thousands of species, or metal, which encompasses hundreds of variations. Leather is in a similar category; the term has been loosely applied to a wide variety of materials possibly only sharing a few characteristics (Thomson 2006). Nowadays, the term leather is used to describe the hide of a vertebrate animal that has been treated in some way so that it resists bacterial degradation, even when wet (Wilson 1931); (O'Flaherty 1958). Other types of hide products, such as those that have been salt cured or have undergone controlled drying to resist biological attack can lose this property if immersed in water. Some oil- or fat infused hides are impervious to the action of water, but they are considered pseudoleathers because their treatment is not truly irreversible (Thomson 2006). Wilson and Merrill say that when a "protein is so altered in composition as to become more resistant to hydrolysis, it is considered to have been tanned, and the material bringing about the change is called a tanning agent" (1931). Tanning agents have varied over the years from infusions of fecal matter of dogs or birds, to vegetable solutions, to brain tanners, to tanning using certain metals or salts, each with varying results and with varying levels of productivity. However, in common among all of these tanning treatments is that they yield a flexible, opaque product, as

opposed to a raw skin that, under uncontrolled drying conditions, will yield a horny, brittle, and translucent material (Thomson 2006). This horny material is most often known as rawhide, whereas the soft material resulting from tanning is called leather.

The physical characteristics of leather

In cross section, most vertebrate hides share remarkable similarities. Starting from the outside, the hide first has an epidermis layer. The epidermis layer consists of 4 layers: the stratum corneum, the stratum lucidium, the stratum granulosum, and the stratum germinatum. The corneum layer is the outermost one; it is characterized by a dehydrated, hard and horny appearance, with cells showing a high degree of degradation, shrinking, and warping. The lucidium is so named because it appears clear, again due to the fact that it is degraded due to dehydration and lack of nutrient input. The granulosm layer exhibits granular damage due to the fact that it is an increased distance away from its supply of blood and nutrients, and the germinatum layer, which is closest to the still-living layers of skin, exhibits primarily intact cellular structure. The epidermis is the part of the skin that is arranged cellularly, rather than according to fibers. The epidermis is totally removed from the skin in the process of leathermaking.

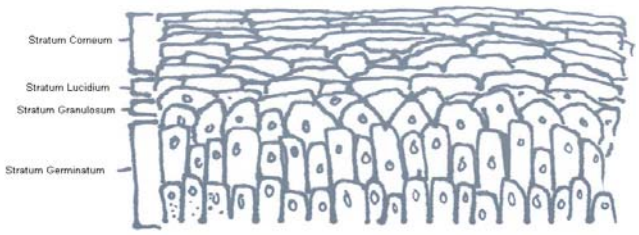


FIGURE 1. The epidermis layer. Vertebrate hides all show similar structures of cellular arrangement in the epidermis layer.

Below the epidermis layer is the dermis, which is the layer used in leathermaking. Starting at the lower boundary of the epidermis, first is the papillary layer, which is composed of fibrous tissue that contains blood vessels, and the base of sweat glands, sebaceous glands, and hair follicles and their associated muscles. Below the papillary layer is the fiber network, which comprises the bulk of leather. It is made of connective tissue fibers, which are in turn composed of collagen fibers, elastin, and fibroblasts. Below the fiber layer is the hypodermis, the skin muscle, and the subcutaneous tissue, all of which are removed in the process of leathermaking (Reed 1966).

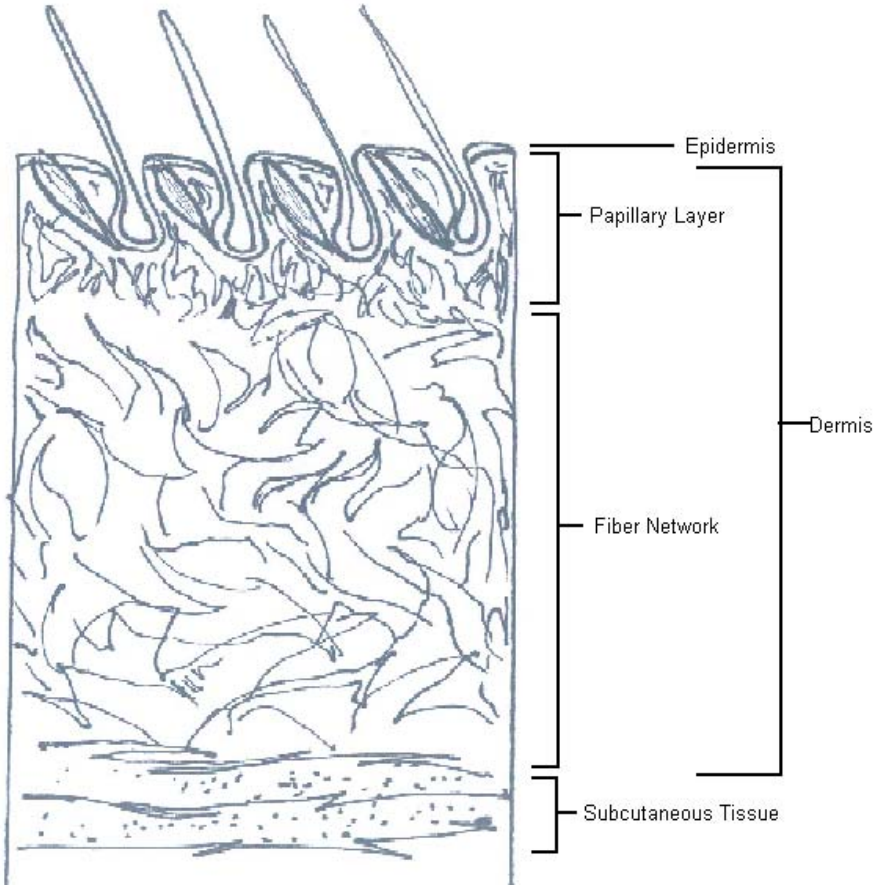


FIGURE 2. Cross sectional diagram of typical vertebrate hide.

Leather chemistry

Collagen is the most important chemical component of leather; it is a protein that occurs primarily in the skin, but also in almost every other tissue and organ in the body, comprising approximately 30% of total body protein mass in man. Like any other protein, collagen is a chain of linked amino acids. These amino acids are linked through a process called condensation in which a water molecule is lost from two adjacent amino acids, thereby forming a protein backbone. All proteins have identical backbones, but

the sequence of amino acids along their length determines their character. Collagen contains 20 different amino acids (Haines 2006). Vertebrate collagen has a generally constant set of constituents: it consists of about 1/3 glycyl residues, 2/9 imino acid residues such as prolyl and hydroxyprolyl, 1/10 hydroxyprolyl residues, and 1/9 alymyl residues. It contains no cystcyl, or tryptophenyl, and only very little methionyl, valyl, histrdyl, hydroxysyl, phenylalanyl, tyrosyl, and aromatic amino acids (Reed 1966).

Collagen chains exist in twisted triple bundles, looking rather like striated yarn. This is due to the fact that there is often appearing in collagen a tripeptide repeat that twists the chain into a coil.

FIGURE 3. The twisted structure of a single collagen chain. Twisted shape is due to its tripeptide repeat.

These coils arrange into groups of three, forming the collagen molecule, also known as the triple helix. These bundles are subsequently gathered into larger fiber bundles which are then gathered into fibers (Florian 2006).

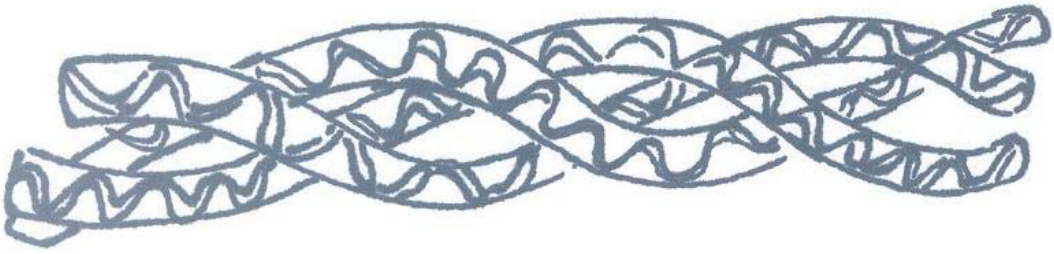


FIGURE 4. The collagen molecule triple helix. Each triple helix is composed of three twisted collagen chains.

Why is leather important in the archaeological record?

Throughout the history of mankind, leather has continually been considered a useful and even vital material. It was the first material that man had access to that could exist in large, tough sheets, and it could easily be used for many different purposes. Leathermaking is often considered to be man's first manufacturing process. Leather has been prized over the years because it is flexible and can be stretched and compressed with little distortion of surface features. It has a high tensile strength, and it is resistant to tearing, puncture, and abrasion. It has a low bulk density and good properties of heat insulation (Thomson 2006). Obviously, it is unique among materials, and was even more so in the thousands of years of mankind's existence before the emergence of plastics and synthetics that could take on similar characteristics. Leather was used for clothing, shoes, tools, furniture, tack, writing material, and shelter. It has played a vital role in many world societies, and has an interesting position of being of use both in the very high and the very low classes. As such, leather articles are imminently useful in the interpretation of cultural heritage.

Unfortunately, leather rarely survives in the archaeological record. Moisture is the essential element of biological degradation, so though leather can remain undamaged indefinitely in totally dry areas, it is rapidly degraded in areas that have variable moisture content (Reed 1972). In fact, the only places where leather has consistently survived in the archaeological record are in totally dry environments, in totally submerged and poorly aerated environments, and in permanently frozen environments. It also survives when in close contact with metals, often due to the transfer of metal corrosion products to the leather to strengthen it (Strzelczyk 1997).

Deterioration of leather

As mentioned earlier, leather in archaeological settings has the paradoxical position of surviving best in extremely dry, desiccated environments and in totally waterlogged environments, but it does not fare as well in temperate areas or those of variable moisture. The reason that leather survives in waterlogged conditions is that presence of large amounts of water and sediment sets up an anaerobic environment around an artifact which most microorganisms cannot tolerate. Additionally, saturated environments promote the formation of compounds that are toxic to many microbial agents, such as methanol, hydrogen, scatol, et cetera (Strzelczyk 1997). However, even if levels of bacterial activity and degradation are nominal, severe deterioration of leather can occur through chemical processes; namely those of hydrolysis and oxidation (Florian 2006).

Hydrolysis

Pure water does not contain only whole water molecules, but also a number of free hydroxyl (OH^-) ions and hydronium (H_3O^+) ions. The hydronium ion breaks bonds in ionic structures, causing them to dissociate. While hydrolysis occurs in relatively low proportions in pure water, it increases dramatically when an acid is added. Acid hydrolysis is similar to hydrolysis—it occurs when an acid is dissolved in water, thereby dissociating into hydrogen ions and some sort of anion. The hydrogen ions react with water molecules to form positive hydronium ions, which cause hydrolysis. Acid hydrolysis is particularly common in nature, because a number of acids are naturally formed from common compounds and atmospheric water. In leather, hydronium ions break the links that join the amino acids in a collagen chain. Since collagen is the most important structural component of leather, this is problematic. One of the major detriments of hydrolysis is that it is irreversible—once damaged, original structural integrity cannot be regained. The most common compound to undergo acid hydrolysis to damage archaeological leathers is sulfuric acid, which is often found in historic leathers because it is an industrial pollution product. There are also a number of other acids that comprise the acidic environment of archaeological leathers; these include organic acids and the deterioration products of amino acid and tannin breakdown. Increases in heat, changes in moisture content, and low pH can speed up the hydrolysis reaction (Florian 2006).

Oxidation

Oxidation is another chemical process by which archaeological leathers deteriorate. Oxidation is defined by laymen to be the combination of oxygen with another chemical compound, such as is the case when iron is oxidized to form iron oxides or rust. However, oxidation is more broadly defined as the loss of electrons from a compound, thereby resulting in the increase of its positive valence. Oxidation can occur due to different types of energy input, including the presence of oxygen, light, heat, or free radicals. Like hydrolysis, oxidation is an irreversible process by which the chemical components of a leather object are fundamentally changed (Florian 2006).

The physical processes by which hydrolysis and oxidation may take place are known as leaching and saturation. In leaching, the water soluble constituents of a leather artifact in a wet burial environment are removed due to the solubilization action of water. Short-chain proteins and carbohydrates are commonly removed from archaeological leather by this process, as are some tanning brines (Strelczyk 1997). Saturation, on the other hand, is an additive process by which materials in the surrounding environment of an artifact set up a uniform and overwhelming microenvironment that soon permeates the entire artifact. In a marine environment, saturation with salt minerals is common. In a non-marine environment, saturation is more likely to take place with iron or sulfides; the products of bacterial action on and around the leather.

Methods of conservation

Fortunately for the conservator, it is often unnecessary to pinpoint the exact type of degradation of a material in order to formulate an appropriate and beneficial conservation strategy. For example, especially in terms of the conservation of organics, extremely similar techniques may be used for the conservation of leather, wood, textile, or bone. There is, of course, nuance to any conservation strategy, but a general discussion of methods that are effective on several classes of artifacts is in order.

There are a number of techniques currently in vogue to conserve waterlogged organic archaeological specimens for further study, display, or cataloging. For leather, all preservation techniques hinge on some sort of alteration to the collagen structure and most do so by removing water. Water is the major component of skin and of collagen, and some water in the structure is free, that is, not chemically bound to the structure of the artifact, and thus able to be removed (Horie 1990). Conservation strategies for leather fall into three major categories: one includes some sort of drying, the other requires the addition of some sort of chemical compound to stabilize the artifact also known as consolidation, and the third involves the treatment of the leather with some sort of bath or dressing that re-hydrates it and protects it. All of these techniques have met with some success and some failure, and the decision as to what will be effective for a particular artifact must be a careful one.

Drying methods

The two most common methods of drying are air drying and freeze drying. As has been previously discussed, air drying is a shaky technique at best. In the case of waterlogged artifacts, any kind of air drying, even under controlled humidity and temperature conditions, will result in irreparable damage to the artifact. Air drying causes fibers of a leather object to force together, resulting in irreversible reactions that will not allow rehydration (Horie 1990). Freeze drying has been much more effective, and often yields a pleasant result from very difficult to conserve or very delicate artifacts. The process has been around for several decades; the first records of freeze drying mention its use in preserving blood samples in the 1930's (Schmidt 1985). It is thought that rudimentary freeze drying was used even earlier by the Incas of Peru, when they would take potatoes to the top of high mountains where they would freeze and the lower atmospheric pressure would result in the removal of some water from their structures (Watson 2004). The process has been perfected over time, and now is often used by archaeologists and conservators. In most cases, the process of freeze drying begins with the addition of some sort of consolidant to an artifact. This is necessary in heavily degraded artifacts, where structural integrity has been lost. The purpose of the added consolidant is twofold: first, it fills the interstitial spaces in the artifact, and second, it prevents large crystals from forming in the cellular matrix of the artifact, thereby possibly causing damage (Jackman 1982). The most common consolidants are polyethylene glycol (PEG) and glycerol. Though PEG was used almost exclusively for freeze drying originally, now glycerol or a mixture of glycerol and PEG is favored, since glycerol does

not have so drastic effect on the appearance of the artifact. Gylcerol acts as a humectant, a consolidant, and a lubricant, allowing leather to retain its flexibility. Glycerol, however, has its own host of problems—it is very dense and hygroscopic, and tends to seep out of artifacts at high heat and high humidity (Randall 2003).

After a consolidant has been added, the artifact to be treated is frozen at -20 to -30 degrees Celsius. This step can be performed in a normal freezer—the purpose is to fix an artifact in its desired position before its final treatment will take place. Finally, an artifact undergoing freeze drying will be placed in a vacuum freezer which is maintained at -18 to -30 degrees Celsius at a pressure of no greater than 150 millitorr. During this process, the remaining water in the artifact is removed and the artifact becomes fixed in its solidified state. The low vapor pressure of the chamber causes any moisture to exit the artifact and move to condensation surfaces installed inside the chamber, rendering an artifact dry and stable. The entire freeze drying process can take anywhere from a matter of hours to months to complete, depending on the size of the artifact and the level of damage prior to treatment (Randall 2003).

Freeze drying is considered to be a fairly effective method of conservation, and particularly in the case of waterlogged leather, it is used almost exclusively by a number of labs around the world. It gives a faithful representation of the artifact with minimal damage or invasion (Cameron 2006). However, it has its own detriments. Many conservators who do not trust freeze drying do so because there is very little control for

the conservator once the treatment has begun. (Schmidt 1985). An artifact cannot be analyzed in terms of treatment effectiveness until post-conservation, and at times, this is simply too late if some sort of damage is occurring due to treatment strategy. In addition, freeze drying can yield an artifact that is highly rigid and unable to be reshaped post conservation. Some freeze drying treatments also vastly increase the brittleness of an artifact. For leather, which might be re-assembled into something like a shoe, saddle, etc., freeze drying may therefore prevent reconstruction, and thus hamper some of the extraction of data from an artifact (Randall 2003). Though freeze drying is currently considered to be the most reliable method for conservation of leathers, conservators in the field would welcome new developments, because of its manifold detriments (Cameron 2006).

Consolidation methods

Early consolidation treatments consisted of dipping artifacts into a hot, saturated solution of alum. The alum helped draw water out of the core of the artifacts, and left a “shell” of solid, treated material (usually wood) on the outside. The main problem with this approach is that it had the potential to completely destroy the core of an artifact, thereby possibly erasing its diagnostic characteristics. At best, artifacts conserved with this treatment were extremely brittle and prone to breakage. At worst, they disintegrated completely in a matter of years (Kaye 1995).

Now, more suitable processes are used. Current trends in consolidation technology lead to two different effects in a treated, final stage artifact: bulking and impregnation. In the process of bulking, some sort of consolidant is introduced that will shore up the weak cell walls or fibers, rendering it stronger without adding too much bulk. In impregnation all of the empty spaces in an artifact (i/e the intercellular spaces, intracellular spaces, and voids due to degradation) are filled with a new material. The most commonly used polymer for either treatment is polyethylene glycol. Of course, there are problems with polyethylene glycol; it tends to become unstable and migrate within or to the outside of the artifact through its pores. PEG is also sensitive to changes in humidity, and it imparts artifacts with a dull brown color and a waxy mien. In addition, PEG will react with the iron in composite artifacts, thereby corroding artifacts from even their waterlogged state. Other agents used for bulking artifacts have ranged from sugar to honey to rosins, with varying degrees of success.

The final method for conservation or waterlogged artifacts that is in vogue today is the use of in situ polymerization. This method is a type of bulking that is an attempt to get monomers, which tend to be relatively easy to manipulate, into artifacts, then polymerize them using some sort of catalysis reaction. This technique is the one most often used by the APRL lab at Texas A&M University.

The use of sucrose as an impregnation agent

In the past, sucrose has been used as an impregnation agent in the conservation of waterlogged wood (Parrent 1983). It proved to be extremely effective for a number of reasons. Economically, it is cheap and easily accessible, able to be obtained in most countries. Many countries that do not have the money to import expensive conservation chemicals in fact refine their own sugar, meaning that the cost of conservation could be doubly lowered. In a practical sense, sugar is an ideal conservation agent because it has a forgiving crystalline structure that is able to easily permeate and support porous materials effectively. The process seems to be fairly reversible, and it imparts no unnatural color or texture to the artifact by the end of conservation. Perhaps most importantly, sucrose treatment keeps an artifact in an aqueous medium during the entire conservation process, which may be important if some diagnostic feature of the artifact could be destroyed by exposure to organic solvents (i.e. organic inks, etc.). In his thesis, Parrent notes that the use of sugar as a consolidant is not a new one—a 1904 US Patent delivered to W. Powell noted that "sugar acts as a binder between fibers, in addition to the mere filling of the interstices, much increasing thereby the solidity in the case of less hard wood, while vulcanizing, strengthening, and toughening all timber, both hard and soft (1983)." The process was then used to preserve barrel staves and railroad ties—though using molasses in most cases rather than pure cane sucrose.

The process by which sucrose is introduced into an artifact is simple: it is added incrementally to an aqueous solution submerging the artifact over a period of time.

Though simple, it is important to note that the replacement of water with sugars must occur slowly in order to ensure that the artifact is not stressed beyond its limits. At the end of treatment, the sucrose-imbedded artifact is allowed to dry, either in air or with the aid of a dessicator.

Though sucrose has proven itself to be effective in the bulking of waterlogged woods, it has not been used at all to conserve other organic materials, such as leather. As such, research is needed to determine whether the bulking of leather with sugars is a reliable and affordable option, especially for countries that do not have access to more advanced and expensive methods of conservation.

The use of silicone oils as bulking agents

A method of bulking that has only recently been used to great effect in the conservation of artifacts is the use of Passive Polymers and silicone oils to conserve artifacts through in-situ polymerization, as earlier noted. The process used to conserve artifacts using silicone oils is theoretically simple. First, a waterlogged artifact is dehydrated using baths of alcohol and/or acetone to drive off all water. The drying agent is assumed to permeate all the cavities in the cellular structure of the artifact. Next, the drying agent is displaced, and some sort of Passivation Polymer is introduced to take its place, typically under vacuum. This Passivation Polymer is a mixture of a silanol terminated polydimethyl siloxane silicone oil with an alkosilane cross linker, such as MTMS (methyl trimethoxysilane), mixed in varying proportions depending on the desired

finished effect for the artifact. Put succinctly, the idea is that the cross-linkers will react with the carbonols (-COH) on the cell surface of the substrate, with each other, and introduced silicone oils, and in such a way provide an interior scaffolding to the structure of the artifact. Finally, the artifact is exposed to a catalyst that serves to fix the polymerization occurring in its cells (Smith 2003). This occurs in three steps: first, there is a spontaneous hydrolysis of the catalyst. In this case, the catalyst used was dibutyl tin diacetate or DBDTA. It reacts with ambient water vapor, resulting in the cleavage of a acetal group and a replacement of said group with a hydroxyl (-OH). Next, there is a reaction between the dibutyl tin acetate hydroxide formed previously and the MTMS cross linker in which the OH is removed from the dibutyl tin acetate hydroxide, and replaced with a trimethoxysilane. Finally, the polymerization intermediate formed in the previous synthesis combines with the silanol-terminated polydimethyl siloxane, in which a trimethoxy silane group is cleaved from the polymerization intermediate and replaced with an alcohol functional group in the silanol terminated polydimethyl siloxane. Thus, the end results of this reaction are a polydimethyl siloxane, a methyltrimethoxysilane, and a dibutlytin acetate hydroxide. (Randall 2003).

Though seemingly chemically complicated, this treatment is highly effective, and does not have some of the drawbacks that more traditional treatments do. It is more permanent, with the polymers in an artifact having a half-life of well over 200 years before they begin to substantially degrade. Silicone conservation also adds very little

weight or bulk to an artifact because rather than fill the intercellular spaces, it acts as internal scaffolding, leaving spaces that were previously vacant still so (Smith 2003).

One significant drawback of a silicone treatment of an artifact is that it is an irreversible process. Those that descry the process almost invariably do so because of this fact, and also because Passivation Polymer technology is such a new technology that very little is known about what its degradation processes will look like, when it finally comes.

The use of leather dressings and baths

One conservation strategy that is neither a drying process or a consolidation process but that which is often used on archaeological and historical leathers is the use of leather dressings or baths. The use of leather dressings and baths is the most traditional method for leather conservation, and frankly, it is still an effective method under certain circumstances, though admittedly it is most generally effective in historical leathers rather than in archaeological leathers. The goal of a successful dressing or bath treatment is slightly different than the goal of a different sort of conservation strategy. Rather than attempt to create a static object by making it impervious to change, a bath or dressing seeks to establish oil, moisture, and acidity levels in a leather artifact that are conducive to long-term stability. Dressings are usually thick emulsions that are topically applied by hand, and baths are thinner solutions into which artifacts are wholly immersed. In waterlogged artifacts, sometimes a dehydration process is necessary before a dressing or bath can be applied, but sometimes, the actual treatment's

hydrophobic nature is depended upon to drive water out of the artifact. Usually, either treatment must be re-applied every few years to ensure that the artifact remains well protected and in good condition (Randolph 2003).

Leather dressings and baths used on wet archaeological leather are usually paired with acetone dehydration to drive off all water (Von Soest 1984). Originally, leather artifacts were treated with dressing until they stopped taking up dressing—this was a method by which all water was removed, but these were found to weep dressing long after treatment. Now, dressing applications are limited to only 4% of the total mass of an artifact—this amount gives good conservation and dehydration results, but still is neat long after conservation (Randolph 2003).

Most leather dressings or baths consist of some or all of the following ingredients:

1. Oil: added to leather to improve moisture content and suppleness. Serves to lubricate leather without adding water to it. The most common oils used in dressings are neatsfoot oil, anhydrous lanolin, castor oil, and cedarwood oil.
2. Buffers: some type of buffer must be added to keep leathers in a safe pH range, which is generally considered to be between 5-7. Since archaeological leathers almost without exception tend to become more acidic with time, traditionally artifacts were treated with a 4% ammonium hydroxide solution to bring up their pH. Now, artifacts are more likely treated by having a mild buffer such as imidazole added directly to their conservation medium.

3. Waterproofing Materials: The most common water repellent that is in leather dressings and baths is beeswax. Even in small quantities, it serves as an excellent and non harmful repellent; though it can sometimes cause stickiness in artifacts.

The most well-known and oft-used of leather dressings is the British Museum Leather Dressing, or BMLD. It consists of 200g Lanolin, 15g beeswax, 30mL cedarwood oil, and 350g hexane. Some later leather dressings have dispensed with hexane in favor of other solvents, since hexane, though extremely effective in terms of solvent properties, can be harsh on artifacts and also dangerous in a lab setting (Randall 2003).

The role of this research in terms of the larger body of academia

Silicone oil technology is new, and thus, is often distrusted by old-line archaeologists and conservators. However, it must be admitted that the use of silicone oils in artifact preservation has yielded extraordinary results. The process still needs to be considered in terms of usefulness and effectiveness, especially in side-by-side comparison with other methods. The goal of this research is to compare the effects of sucrose as a conserving agent in leather to silicone oil as a conserving agent of leather. While there has been a good deal of work completed with the use of silicone oil in that medium, there has been no study concerning the use of sugars, and it bears analysis, especially since it is a cheaper conservation strategy that does not require complex dehydration methods.

The benefit of this research is twofold. First, it will compare silicone oil treatments with a method of conservation to which it has not been previously compared. Though a good deal of study has been conducted on the differing effects of silicone oil treatments and PEG treatments, no comparison has been made between the effects of sucrose impregnation to silicone bulking.

Secondly, this research will have the effect of testing a brand new type of conservation strategy. Since sucrose has never been used in the conservation of leather, it will be useful to have basic idea of what its effects will be on this material. For this branch of research, it will be instructive to have parallel silicone oil treatment of similar artifacts under similar conditions because the excellent yield of the silicone oil treatment will serve as a good baseline by which to judge the effectiveness of this new form of treatment using sucrose.

CHAPTER II

METHODS

Experiment I: Comparisons of silicone oil methods and sucrose impregnation methods of conservation

First, pieces of leather of similar size were selected from stock sources, namely those used by D. L. Hamilton's conservation class at Texas A&M University. Four pieces were chosen to represent each conservation strategy and four were chosen to serve as a control. Each piece of leather was removed from water, patted dry, and then measured with digital calipers (length, breadth, height) then traced. Additionally, any particular identifying marks were noted. Finally each piece was photographed front and back, then returned to water. It was not deemed necessary to identify each piece with a number due to the fact that they were easy enough to identify on an individual basis that such a designation would have been immaterial.

Silicone oil conservation

Dehydration

Four pieces of leather were placed in 100% Ethanol to begin dehydration process. It should be noted that a less stringent dehydration might be more effective with more highly degraded artifacts; i.e. a quantized step up from 50/50 Ethanol/water to 75/25 Ethanol/water to 100% Ethanol. Since these artifacts were in relatively good shape, it was assumed that they could easily withstand a rigorous dehydration process. Fast

dehydration may cause leather products to shrink (Jackman 1982). A slight vacuum was applied, then soon turned off to allow the artifacts to stand at ambient pressure. After 1 hour, the vacuum was repeated, and artifacts were again allowed to stand for 1 hour. At the end of this period, artifacts were removed from 100% ethanol and placed in 100% acetone. Vacuum process was repeated exactly as it was carried out while in ethanol. Finally, all old acetone was removed and replaced with fresh acetone at ambient temperature and pressure and allowed to stand for 5days.

Preparation of silicone oil solution

A base solution of PA oil (a low viscosity silicone oil) with approximately 7-10% (volume/volume) MTMS was used. This stock solution was one that had been recycled already by other conservation students, so fresh MTMS was added in order to ensure a properly active solution. For the purpose of this project an exact MTMS percentage was not necessary. However, a solution containing a low percentage of MTMS will yield a more pliable, flexible polymer than one with a high percentage of MTMS, so decisions as to solution strength must be made accordingly. The solution was then checked for activity by placing a small amount in a tin tray with a few drops of catalyst. An increase in viscosity showed that the solution was active, since some catalyzation (and thus polymerization) was taking place.

Treatment

Artifacts were entirely submerged in the silicone/MTMS mixture. They were covered with fine wire mesh and weighed down to ensure that they would remain totally submerged for the duration of treatment, since exposed portions often end up not fully conserved. A slight vacuum was applied, then turned off, and the solution was allowed to stand for 24 hours. Vacuum was subsequently reapplied, relieved, and artifacts again stood for an additional 24 hours at ambient temperature and pressure. After the full 48 hours, samples were exposed to vacuum twice in a 1 hour period, then were removed from silicone and allowed to stand on wire mesh to drain excess oil from their surface. They stood for approximately two hours, then underwent surface treatment with MTMS to remove residual pooling silicone oil, then were surface cleaned with lint-free lab wipes. Over the next three hours, these samples were periodically checked for drainage, then cleaned and MTMS treated.

Catalysis

Finally, samples were placed in a sealed container with a small well of DBTDA catalyst and allowed to stand for 48 hours. Used catalyst was removed and disposed of, and fresh catalyst was added, this time with artifacts resting on metal mesh above the catalyst to ensure complete catalysis of all surfaces. Again, samples were allowed to stand for 48 hours, then used catalyst was removed and disposed of, and new catalyst was again added to the container. The artifacts were turned this time to ensure that they catalyzed fully on both sides.

After 24 hours, the used catalyst was removed and the artifacts were removed from the sealed container and allowed to stand. A white crust was visible on the surface of the artifact due to vapor deposition of the catalyst, so two of the four treated artifacts were mechanically cleaned with a soft brush until the crust was removed. The crust was allowed to remain on the other two. All four samples were photographed, measured, and weighed.

Preparation of samples for analysis

Thin sections of this material were prepared by hand using microtome blades for analysis using SEM and bright field microscopy. For bright field microscopy, these sections were placed on glass without fixative to be viewed. For SEM, these were oven dried, sputter-coated twice with carbon, then painted around each edge with a conductive paint. This somewhat excessive treatment of SEM samples was due to the fact that in the first attempt at analysis, these samples did not ground properly, and thus the SEM was unable to obtain a picture or a relatively accurate EDS.

Sucrose conservation

Four pieces of leather of similar size were chosen to undergo sucrose treatment. They were placed in a 10% w/v solution of sucrose (i.e. 50g sucrose brought to 500mL with tap water) and allowed to stand for 48 hours.

Approximately 350 mL sucrose solution was then removed from the container (enough to provide a high volume for further dissolution, but so that enough was left in the original container to cover the samples) and an additional 50 g sucrose was added, under slight heat and stirring to put it in solution. When returned to the main solution in the original container, this brought the sample to approximately 20% w/v.

This process was repeated every 48 hours until a solution strength of 50% is reached. Once the solution has reached 50% w/v with no apparent ill effects to the artifact, the final stages of sucrose addition can be enacted rapidly; (ie 35% over 48 hours.) This solution was allowed to stand for the next four days, until floating leather pieces increased their sucrose uptake to the point that they would sink, now in equilibrium with their environment.

Finally, these samples were removed from sucrose solution and placed in a fume hood to dry. They were monitored over the next 48 hours. At the end of this time, any sucrose that had pooled and hardened on the surface of the artifact was removed using dampened cotton swabs. Care was taken not to saturate the object with water, since this would certainly remove some of the sugar from the artifact, thereby rendering it less stable. Finally, samples were photographed, measured, and weighed.

Preparation of samples for analysis

Thin sections of this material were prepared by hand using microtome blades for analysis with bright field microscopy. For bright field microscopy, these sections were placed on glass without fixative to be viewed.

Standard samples

4 samples were chosen to serve as standards without any sort of treatment, each was recorded, photographed, and measured. Two served as dry standards; both were dried in the hood. These samples were used to help estimate the water content of all of the samples. Two samples were also preserved as wet samples; one was sectioned for viewing with SEM, and the other was left in water for the duration of the treatment to serve as a wet control.

Preparation of samples for analysis

These samples were prepared for analysis in the same manner as those undergoing Passivation Polymer treatment: some were prepared for SEM viewing by being sectioned, oven-dried, sputter-coated with carbon, and painted with conductive paint. The sections for bright field microscopy were prepared by being hand cut and placed on slides without fixative for viewing.

Comparative analysis of samples from differing treatments

In addition to being compared using general aesthetics and measurements, these samples were compared visually using bright field microscopy and were thoroughly analyzed using SEM. Though the mechanisms of bright field microscopy are well enough known to not merit a discussion, a short discourse on the operation of SEM is necessary to facilitate understanding of results obtained thereof. A Scanning Electron Microscope operates by using an electron beam to irradiate a sample that is prepared specifically to be able to withstand it; typically by coating with some sort of material protective material. The coating material of sample can range from a gold-palladium sputter-coat to a simple carbon coating, and is based on what will give the most appropriate image and analysis for the artifact at hand.

When the beam of electrons is incident on the artifact, some electrons transmit through, and are then scattered at a well-defined angle, depending on the material that they hit. X-rays are produced when the electrons entering the sample act on the innermost electron shell of the atoms of the sample. These electrons in the inner shell are ejected and a hole is produced that is subsequently filled with an outer shell electron. This transmission from outer shell to inner shell produces x-rays of characteristic energy, depending on the element of the atom (José-Yacmán, 2000). An EDS is a tool of SEM that quantitatively measures the magnitude of x-rays on a silicon/lithium detector, thereby allowing an estimation of the relative amounts of different elemental components in a sample. In order for an EDS to be most accurate, a sample must be

prepared by polishing the surface to a uniform finish so that there is no variation in reading based on topography. For the purpose of this research, this step was deemed unnecessary, since obtaining exact quantitative data would have been excessive. Instead, EDS was taken at several points through the cross section of the artifact, and the ratio of silicone to tin was compared in order to see how far into the artifact the catalyst had traveled, and in what direction.

Experiment II: A side-by-side comparison of the effects of differing silicone oils and catalysts

Sample preparation

In order to more fully understand the mechanisms and nuance of silicone oil conservation, a second project was carried out to compare the effects of different viscosities of silicone oils in artifact preservation. This experiment was carried out on seven modern, dry leather samples, each of which had undergone a slightly different process of tanning, thereby yielding different results in terms of color and flexibility. Each of the seven samples was cut into three similar pieces; one to serve as a dry control, one to undergo treatment with a medium viscosity Q1 oil, and one to undergo treatment in a low viscosity PA oil. The three groups were designated A,B, & C, and each piece had a number within its group, 1-7. Thus, artifacts were noted by 1A, 2A, 1B, 2B, etc. The pieces were extensively photographed, measured with digital calipers, and weighed.

Solution preparation

PA oil was prepared with approximately 10% w/w MTMS, and Q1 oil was prepared with 5-8% w/w MTMS. This disparity in MTMS concentrations will help to make the end products more similar in flexibility, since MTMS can make an artifact more rigid on its own, without the intervening action of a catalyst. Thus, a smaller amount of MTMS is mixed with a more viscous oil, and vice versa. These solutions were both tested for activity by adding a few drops of DBTDA catalyst to each and observing for a resultant increase in viscosity.

Treatment

Artifacts 1A-7A were placed in Q1 silicone oil solution, and 1B-7B were placed in PA silicone oil solution. Since these artifacts were not saturated with extremely light acetone as those in Experiment 1 were, it was less likely that they would float in their treatment solution, and thus, it was not necessary to fit the containers with screen and weigh them down as it was in the previous experiment. A slight vacuum was applied to both baths, then both were allowed to stand at ambient pressure for 24 hours. At the end of this period, a vacuum was again applied, and the artifacts were again allowed to stand for an additional 24 hours. Finally, these samples were removed from silicone oil and allowed to stand for approximately 5 hours. They were then turned, and allowed to drain overnight.

The next day, silicone treated artifacts were examined for surface pooling, then surface cleaned with MTMS.

Catalysis

These artifacts were placed in air-tight, sealed containers, resting smooth side up on fine wire mesh over a tin tray containing a small amount of DBTDA catalyst. They were allowed to stand for 24 hours, or until the catalyst was assumed to have depleted its activity. Used catalyst was then disposed of, and fresh catalyst was added. Samples were turned over, (nap side up), and samples were again allowed to stand for 24 hours to continue catalysis. This process was repeated a third time, this time with smooth side up.

After three catalysis treatments using DBTDA were applied, these samples were analyzed for completion. They exhibited some level of stiffening, but still exuded silicone oil when slight pressure was applied. Based on this evidence, it was deemed that the catalyst used for these samples was past its usability, so fresh TPT titanate catalyst was used. TPT titanate was introduced in the same manner as DBTDA catalyst was: it was placed in a tin tray below the samples resting on fine wire mesh, then sealed in an air-tight container. At the end of the 24-hour treatment period, these samples were observed to have a coating of liquid catalyst due to the fact that vapor deposition continued to the point that it condensed on the artifact. This is not a favorable condition for catalysis, so these artifacts were surface cleaned carefully with paper towels. Next,

the samples were allowed to stand for several hours to see whether catalysis was complete. At the end of this time period, they were found to be still damp, so were re-catalyzed by being placed again in an air-tight container, over a tin tray containing a small amount of catalyst soaked into a cloth.

Analysis

Each finished sample was photographed and recorded in terms of dimension and weight. Each was also analyzed in its finished state and compared in terms of properties of flexibility, texture, change in color, and general appearance.

Experiment III: An exploration of the mechanism of sucrose treated samples

After initial analysis of sucrose treated samples, it was deemed that a more aesthetically pleasing result might be yielded from samples that did not undergo a full sucrose treatment, but rather were stopped at a lower level of sucrose saturation. The goal of this trial was to reach a happy medium between shrinkage, which should occur more drastically at low concentrations, and stiffening, which should occur more drastically at high concentrations. For this experiment, 14 pieces of waterlogged leather were cut from a single continuous piece chosen from D.L. Hamilton's stock solutions. These pieces were extensively photographed, measured (length, breadth, and height) and were weighed. 4 were chosen to serve as dry controls; they were placed in a fume hood to fully dry. The rest of the samples underwent similar treatment to those in Experiment I, i.e. They were started in a 20% w/v solution of sucrose then 10% was increased every 24

hours until 80% was reached. However, for the purpose of this exercise, one sample was removed each day immediately prior to the treatment, and allowed to dry in the fume hood. Thus, at the end of this experiment, there was one piece of leather containing 20% sucrose, one containing 30%, and so on, until four containing 80% sucrose.

Once each piece dried completely, it was photographed, weighed, measured, and drawn.

Analysis of samples

These samples were analyzed according to their flexibility and texture before and after treatment. Percentage of dimensional change was calculated based on the dimensions recorded prior to and after sample treatment.

Experiment IV: A continued exploration of the mechanism and reversibility of sucrose treated samples

After analyzing the resultant products of Experiment III, it was decided that a further exploration of the mechanism of sucrose treatment might be in order. As a result, a similar experiment was designed with similar parameters. Again, all articles were placed in a container of water, and sucrose was added incrementally from 10% w/v to 80% w/v. The differences in parameter here are that rather than a rapid addition, this time each increment was allowed to stand for at least seven days before the next was added. In addition, three different types of leather were used: one thick and of similar variety to that which was used in Experiment 3, one thin and rigid pigskin similar to

what would be used in bookbinding, and one thin and pliable similar to glove leather. At the end of treatment, one of each of these types of leather were treated with each percentage of sucrose, from 0% to 80%. Then, all samples were measured, weighed, and photographed.

Analysis of samples

These samples were analyzed according to their flexibility and texture before and after treatment. Percentage of dimensional change was calculated based on the dimensions recorded prior to and after sample treatment.

CHAPTER III

RESULTS

Experiment I

Silicone treated artifacts

Visual inspection

Silicone treated artifacts exhibit some level of stiffening, though they are still pliable to a certain extent. Where overexposed to catalyst, they exhibit a white “frost” coat that can be removed with mechanical cleaning using soft brushes. Some darkening is evident with these artifacts, but the diagnostic characteristics are highly evident even after conservation. These artifacts were much more faithful to natural texture and flex than were air dried samples, and the nap on the flesh side of the leather maintained both softness and flexibility.

Bright field microscopy

Under bright field microscopy, silicone treated artifacts exhibit a pleasant mien. They show no shrinking and minimal darkening, and structures are easily visible. If anything, some of the fibers seem more turgid than they might actually be in a natural state, due to the bulking action of the silicone.

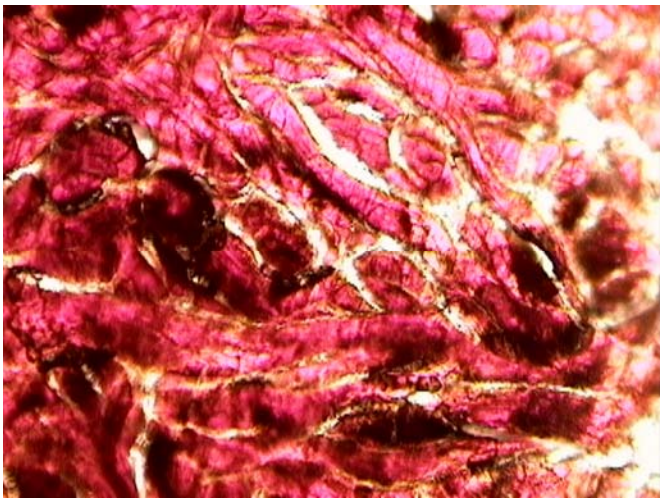


FIGURE 5. Silicone treated leather under bright field microscopy.

SEM analysis of artifacts

The SEM analysis of these artifacts showed first that there was a tremendous difference in structure between the artifacts treated with silicone and the dry controls, much as was to be expected. The dry artifacts had shrunk considerably; their structure was dense, shriveled, and appeared emaciated. The silicone artifacts, on the other hand, showed structures that were still turgid and well supported due to their consolidation treatments.

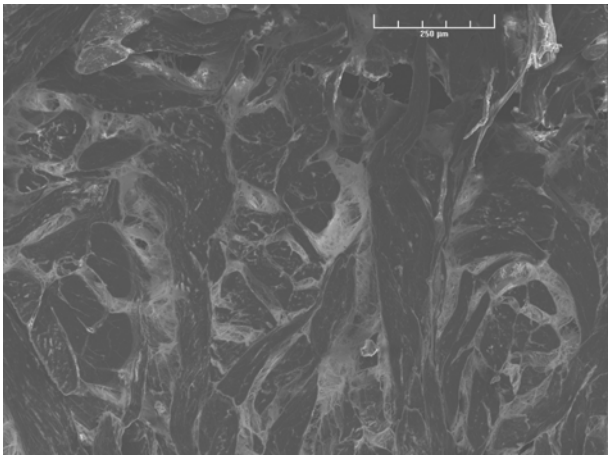


FIGURE 6. SEM of dry control sample. Oven dried and viewed at 100X with SEM.

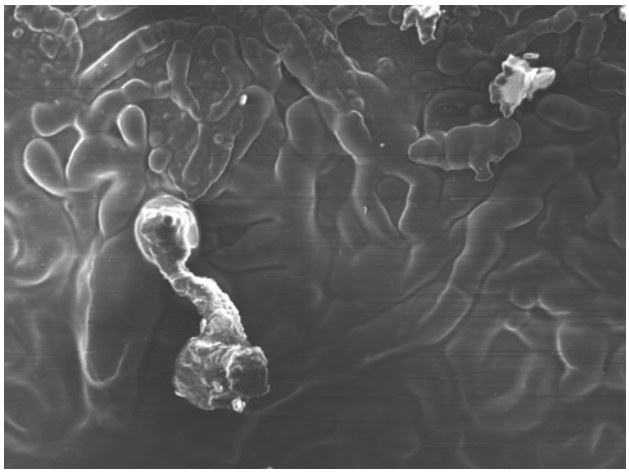


FIGURE 7. SEM of silicone treated leather. Viewed at 100x.

When viewed with EDS scatter, the artifacts showed that there was a higher amount of silicone and drawn into the centers of the fibers, and less around the edges.

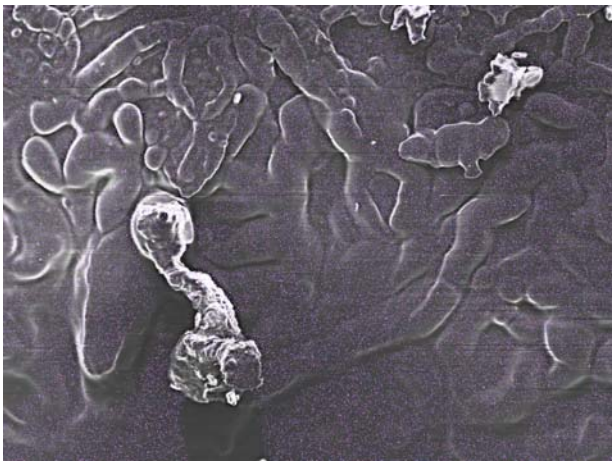
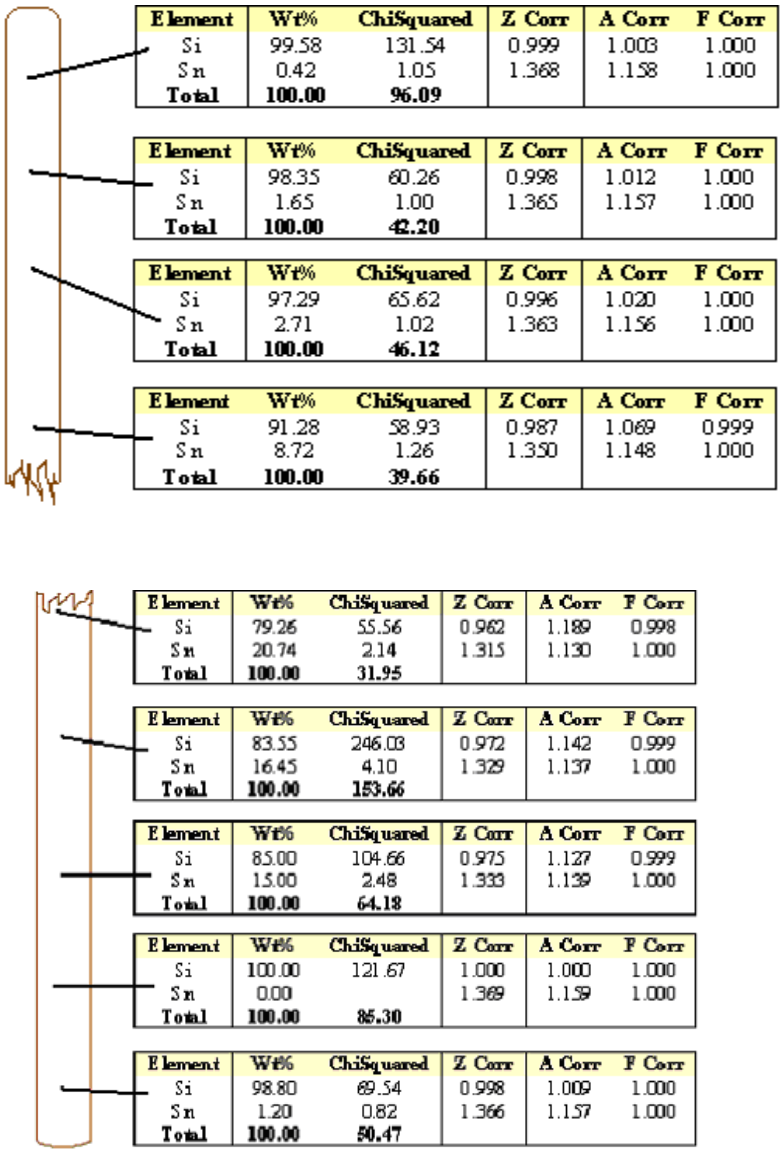


FIGURE 8. SEM of silicone treated leather overlaid with EDS scatter. Viewed at 100x.

This indicates that as treatment continues, the silicone will tend to stay in the most dense areas that it entered, and will tend to migrate more quickly from the less dense areas. This is not a problem conservationally speaking; as long as silicone exists to some degree in the entire artifact, it will be stable. However, it should be taken into consideration to account for the fact that heavily degraded artifacts that are not dense will act very differently under silicone oil analysis than will dense, little degraded artifacts that have much of their structural integrity preserved.

Perhaps the most interesting and unexpected of the phenomena that were observed in an EDS analysis of the artifacts is that in cross section, these artifacts showed the tin to decrease from the nap side of the artifact to the smooth side. On the uncleaned artifact, the nap side showed about 22% tin in relation only to silicone. This decreased then to 16% to 15%, to just over 1%, to about 5% at the cortex surface of the leather. Though the artifacts were exposed to the catalyst on both sides, there are a number of reasons

why this gradient would be in place. First, the nap side of the hide exhibits much more surface area, which means more sites of activity. The nap was the first side to undergo catalysis suspended over the leather, meaning that the chemical processes introduced at this point continued even afterward, and affected the reactivity of the later applied catalyst. Finally, since the catalyst was applied nap side first, it is possible that the catalyst was beginning to lose its activity toward the end of treatment, and thus did not fully complete catalysis on the smooth side of the leather, which was exposed to catalysis later. This last explanation is likely, since later experimentation found that the DBDTA catalyst that was originally used for Experiment I was no longer active for Experiment II. While all of these observations are significant in understanding the mechanisms by which the silicone oil treatment operates, they are not vital to the comparison between silicone oil treatments to sucrose treatments. The final product was still a finished artifact, and had undergone satisfactory treatment.



Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	99.58	131.54	0.999	1.003	1.000
Sn	0.42	1.05	1.368	1.158	1.000
Total	**100.00**	**96.09**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	98.35	60.26	0.998	1.012	1.000
Sn	1.65	1.00	1.365	1.157	1.000
Total	**100.00**	**42.20**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	97.29	65.62	0.996	1.020	1.000
Sn	2.71	1.02	1.363	1.156	1.000
Total	**100.00**	**46.12**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	91.28	58.93	0.987	1.069	0.999
Sn	8.72	1.26	1.350	1.148	1.000
Total	**100.00**	**39.66**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	79.26	55.56	0.962	1.189	0.998
Sn	20.74	2.14	1.315	1.130	1.000
Total	**100.00**	**31.95**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	83.55	246.03	0.972	1.142	0.999
Sn	16.45	4.10	1.329	1.137	1.000
Total	**100.00**	**153.66**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	85.00	104.66	0.975	1.127	0.999
Sn	15.00	2.48	1.333	1.139	1.000
Total	**100.00**	**64.18**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	100.00	121.67	1.000	1.000	1.000
Sn	0.00		1.369	1.159	1.000
Total	**100.00**	**85.30**			

Element	Wt%	ChiSquared	Z Corr	A Corr	F Corr
Si	98.80	69.54	0.998	1.009	1.000
Sn	1.20	0.82	1.366	1.157	1.000
Total	**100.00**	**50.47**			

FIGURE 9. Cleaned, oven-dried leather (top) and uncleaned, oven-dried leather (bottom). Note the percent weight of the silicone oil versus the tin. The extent to which tin permeated the artifact indicates the amount of catalyst compared to the amount of silicone at that particular point. Of most interest is the fact that both are much more fully catalyzed on the nap surface of the leather than on the other.

Sucrose treated artifacts

Visual inspection

Sucrose treated artifacts, under initial visual inspection, appear to be of a similar nature to silicone treated artifacts. Like silicone treated artifacts, they appear slightly darkened, but essentially correct in hue. They still exhibit essential diagnostic features, and were texturally similar to what they ought to be. It should be noted that some features, such as the finest features of nap on the flesh side of the leather are obstructed post sucrose treatment, probably due to the fact that some amount of shrinking occurred with drying causing the fibers to draw more closely together and matt down.

One major dilemma associated with the results of the silicone treatment is that the sucrose treated artifacts exhibited no flexibility after conservation; they were rigid and somewhat woody. While this may be acceptable for an artifact that will be going immediately to display, it is more problematic for one that needs to undergo study.

Bright field microscopy

Perhaps more concerning than the rigidity of the post conservation artifact is the fact that artifacts treated with sucrose still show some (if minimal) shrinking and warping under bright field microscopy.

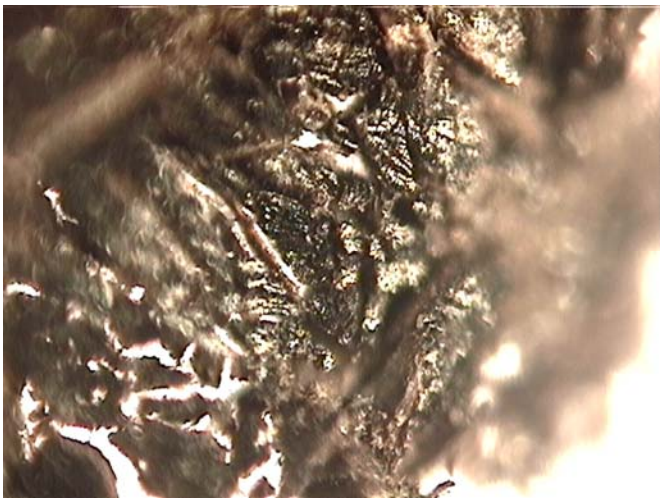


FIGURE 10. Sucrose treated leather under bright field microscopy. Note that it is substantially darker than silicone treated leather under bright field microscopy, and that it exhibits some separation of fibers.

This is most evidenced by a slight separation of fibers, particularly near the outer edges of the artifact. This is most likely attributable to wet surface cleaning post conservation, which may have easily drawn some of the sucrose bulking agent out of the artifact. This should serve as a warning for anyone who employs this conservation strategy in the future: obviously artifacts must remain in a humidity controlled environment to maintain their integrity, and particular care must be taken when surface cleaning these artifacts to ensure that they are exposed to as little water as possible.

Dry standards

Visual inspection

The dry standards created by extended exposure in the fume hood behaved almost exactly as was to be expected. They shrank and warped substantially, and exhibited some exfoliation along planes in cross section. They also darkened slightly in color and exhibited considerable change in both texture and flexibility. The sample became totally rigid post-conservation, and also the nap of the flesh side of the leather exhibited such shrinking that no individual fibers were visible any longer.

Bright field microscopy

A thin section under bright field microscopy showed that substantial shrinking had occurred, thereby drawing the fibers away from each other and leaving large voids throughout the artifact. This is obviously problematic, since it leaves the artifact in a highly damaged, weakened, and changed state.

FIGURE 11. Air Dried leather under bright field microscopy. Note the dark appearance and total separation of fibers from each other.

TABLE 1

Comparison of Physical Properties of Treated Leather

	Flexibility (1-5, 5 being original waterlogged state	Texture (1-5, 5 being original waterlogged state	Resistance to Humidity (1-5, 5 being highly resistant	Reversibility (1-5, 5 being totally reversible)
Waterlogged	5	5	--	--
Dry Control	1	2	2	1
Sucrose Treated	2	3	2	1
Silicone Treated	3	4	5	4

Experiment II

The results of Experiment II were surprising in some ways, but they also helped to illuminate some of the questions that arose as a result of Experiment I. Aesthetically, the leather following both treatments was similar. Artifacts in Group A exhibited more

stiffness than those in Group B, but this is probably due as much to the method of application of catalyst to the fact that it was a more viscous catalyst. Under catalysis with DBTDA, artifacts did not set properly. Granted, they did stiffen some, but they also were extremely damp and exuded silicone oil post catalysis. As a result, a stronger, titanium based catalyst was used, which set the artifacts nicely. The first application of the catalyst yielded artifacts that were coated with catalyst; obviously this is not a favorable condition for real artifacts. The coating was due to the fact that more catalyst than was strictly necessary was used and the container it was placed in was completely airtight, meaning that vapor catalysis quickly led to the artifacts serving as condenser surfaces. The fact that the catalyst applied itself directly to the artifacts means that they ended up stiffer than might have been the case if only vapor catalysis had taken place; a higher percentage of catalyst in the surface was probably detrimental. The second application of catalyst was vapor only; a small amount of catalyst was applied to a lint-free cloth and placed in the container housing the artifact.

When removed from catalysis treatment, these artifacts showed pleasant results. They were dry to the touch and still retained a high level of flexibility and fiber integrity. Though they did in fact darken with treatment, surface detail was still evident. This darkening may be immaterial for waterlogged leather, since it is almost invariably darkened pre-conservation due to oxidation, and presence of irons, tannins, or sulfides (Cameron 2006). Since these samples were new and non-waterlogged at the beginning of treatment, no shrinkage should have occurred. However, slight variations in

measurement from before and after treatment can be seen; these can probably be attributed to the compressibility of the samples while using calipers both before and after treatment.

FIGURE 12. Representative sample of silicone treatment pre- and post treatment. Notice change in hue with the treatment.

Experiment III

Visual analysis

Aesthetically, the samples used in experiment III yielded surprising, but highly explainable results. Upon total drying, it was discovered that the raw material used in this trial was not as degraded as some of the previously used raw material. Granted, it did shrink and warp to a certain extent under air drying, but it still retained flex afterward, a property that is unheard of with actual leather artifacts that have undergone higher levels of degradation. The upside of this is that the uptake of sugar could be tracked, so to speak, in finished artifacts based on their ending stiffness, since those

artifacts conserved with sucrose obviously lost their flexibility as their crystalline structure was fixed. With this being said, it was quickly obvious that there was a marked difference between the artifacts conserved with up to 40% sucrose, and those that had between 50% and 80% sucrose. The samples up to 40% showed very little darkening, and still retained their flex. Those at higher percentages darkened considerably and were rigid. It must be noted, however, that some darkening is bound to occur with any conservation strategy, no matter what is used. To the credit of this treatment, the diagnostic attributes were not lost even after conservation; though the leather had deepened in hue, features remained distinct. In favor of the higher percentage treatments is the fact that these artifacts showed little or no signs of warping, as opposed to the smaller percentages which warped substantially. Dimensionally, these artifacts behaved disappointingly. There was no traceable pattern to the amount of warping or shrinking that occurred, rather, artifacts at all levels of sucrose impregnations changed dimensions erratically. This indicates that the fast treatment and drying used here may not be the best option for the well-being of these artifacts.

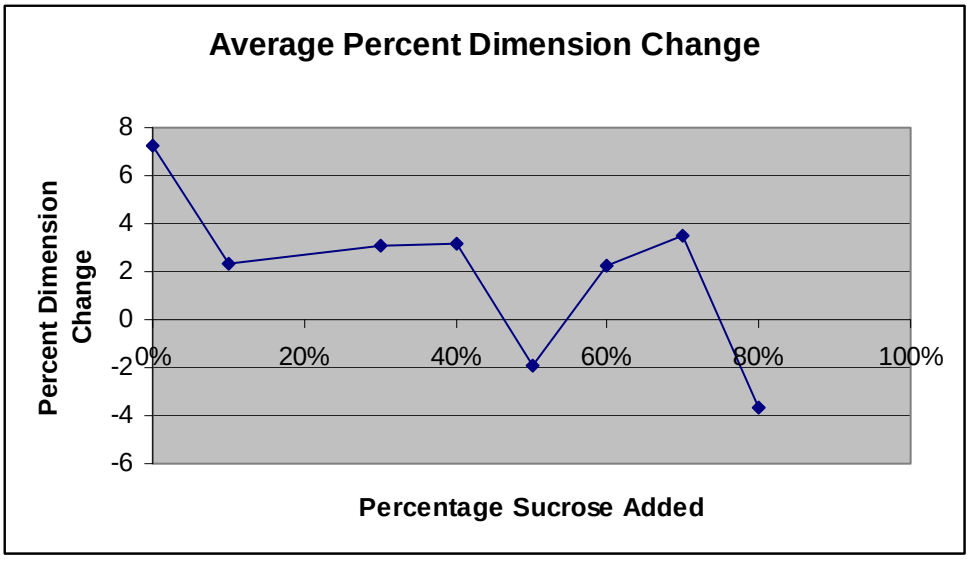


FIGURE 13. Graphic representation of average percent dimension change. Note erratic, but small dimension change from approximately 20% sucrose to 80% sucrose.

Bright field microscopy

The dry control sample, under analysis with bright field microscopy, showed itself to be rigid, firm, and brittle. It had a sheen due to its quick and uncontrolled drying, and the individual fibers had begun to separate. Upon separation, these fibers damaged themselves irreversibly; strands of some could be seen clinging to their adjacent neighbors and pulled away from the bundle to which they belonged.

Samples that were treated with sucrose showed two different faces: Those with a smaller percentage of sucrose (e.g. 20%-40%) showed a surface in which the individual crystals were still obvious. These samples had a grainy appearance, and though some of the larger, more permeable features had filled more fully with sucrose, in generally, they

were not entirely consolidated. This shows that while a smaller percentage of sucrose may yield an artifact that appears to be stable, there is a good chance that it will degrade later due to the fact that it is not fully consolidated, and thus, not fully conserved. Additionally, this shows that an artifact that is only nominally degraded as these were may fare well with such a gentle treatment, but something more stringent may be necessary for artifacts that are more degraded and less stable. Another aspect that must be considered is that at solutions over 40-50%, sucrose naturally inhibits microorganism growth because it is at too high a percentage for survival. However, at theses lower percentages, it loses these inherent biocide properties, meaning that a biocide must be added separately if these artifacts are to be stored safely.

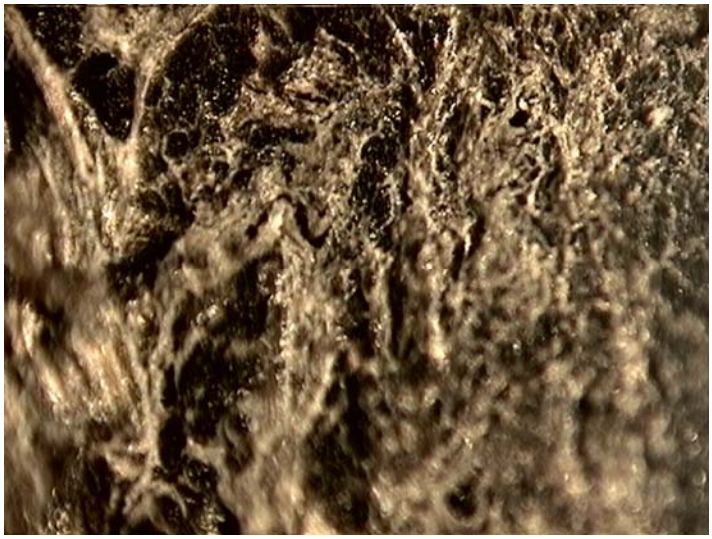


FIGURE 14. Leather treated to 30% with sucrose. Note grainy texture, in which some individual sugar crystals can be discerned.

Samples that were treated with 50%-70% sucrose showed solidity throughout their entire structure, indicating that the sucrose solidified into a unified structure, rather than individual crystals. While this is beneficial in that it indicates that the samples were fully consolidated and thus likely to be structurally stable, it also means that there is some added bulk and loss of flexibility in the finished artifact. This state may be detrimental if reconstructions or further analysis should take place at the end of treatment, but it may be of no consequence if artifacts are simply to be displayed.

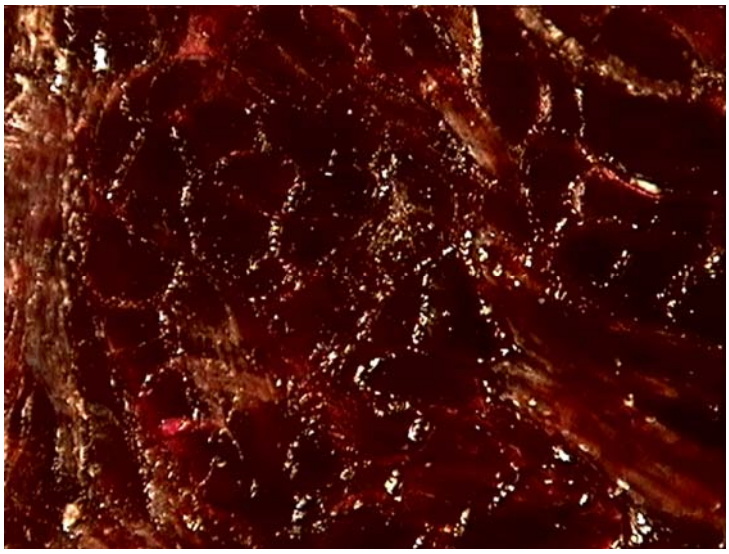


FIGURE 15. Leather treated to 60% with sucrose. Note glassy appearance, in which no individual crystals can be discerned.

Experiment IV

Experiment 4 was carried out in order to rectify some of the problems that emerged in Experiment 3. Chief among these was that the rapid sucrose impregnation process used

in Experiment 3 led to uncontrolled drying, which in turn caused all objects to warp and change in dimension.

Visual inspection

Under visual inspection, the artifacts conserved with sucrose showed similar results to those in Experiment 3. Those up to 30 to 40% still exhibited flexibility, whereas those at higher percentages of sucrose impregnation stiffened substantially. The stiff bookbinding leather was less likely to show a substantial stiffening, since it was already partially rigid. Other, more pliable beginning products showed more stiffening.

All artifacts, as expected, showed some darkening. Additionally, those that were conserved with high percentages of sucrose showed some surface pooling of solid sucrose.

When dimensional change was averaged for each level of conservation, it was found that the lowest levels of shrinking occurred at approximately 40% to 60%. This is fortunate, since at these levels, artifacts still have some pliability. It would seem, therefore, that this particular level would be most beneficial for these artifacts.

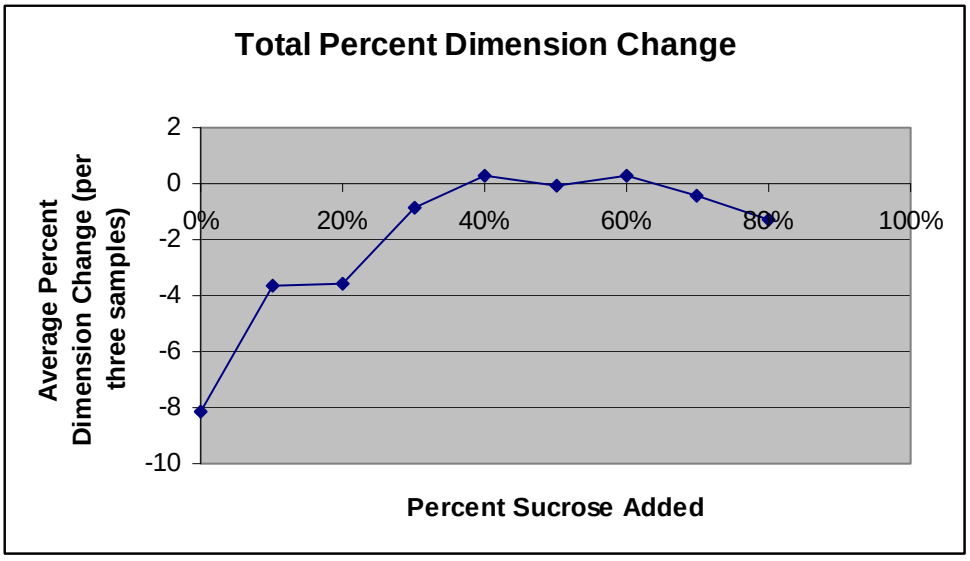


FIGURE 16. Graphic representation of average percent dimension change. Note that the smallest amount of dimension change occurs at approximately 40%-60% treatment.

The dilemma that comes as a result of this conclusion is that the optimal percentage of added sucrose would be different depending on the level of degradation prior to the beginning of treatment. Thus, to achieve the best results every time, some method of determining the approximate level of degradation must be employed. Additionally, a sucrose level this low would not act as a natural biocide, so a different biocide must be added in order to limit pest infestation.

CHAPTER IV

SUMMARY AND CONCLUSIONS

The use of silicone oil as an agent for conservation continues to prove itself superior to other treatments under close analysis. Silicone treated artifacts are highly stable and are faithful to both their original waterlogged condition and the presumed original state. The technique is versatile and allows the conservator a high level of control throughout all steps of conservation. The product is aesthetically pleasing, flexible, and texturally correct, and thus represents an ideal standard for a responsible conservator.

In sucrose impregnation treatment, though sucrose penetrated the artifacts fully and acted as an adequate bulking agent, it had a number of problems associated therewith that cannot be ignored. It yielded a dark, dry and texturally unyielding artifact, one that, though similar in appearance to its silicone treated counterpart, showed a higher sensitivity to humidity and handling. Though sucrose treatment was reversible, it probably has at least some drying effect on the artifact that cannot be overcome or corrected, as well.

Benefits of sucrose bulking

Foremost in the list of merits of the use of sucrose for the conservation of leather artifacts is the fact that it is an extremely cheap process and one that requires no particularly special sorts of materials. Tap water can be used rather than deionized water, and containers in which artifacts are to be treated can be scrounged from almost

anything. Relatively pure sugar in the form of table sugar is available almost anywhere, also cheaply.

Artifacts conserved with sucrose seem to be faithful to their original states, at least visually. They are darkened and dried to a certain extent, however, no more so than artifacts conserved with some other treatment processes. Since so many museums or facilities use no formal conservation process at all, but rather allow their leather artifacts to simply dry out in air, sucrose impregnation is, of course, a better alternative to this highly irresponsible practice.

Perhaps most importantly in terms of the benefits of sucrose bulking is that it seems to be an extremely reversible process. Though there is some drying which causes irreversible damage, it is not to such an extent that it makes the process not worthwhile to consider. However, all told, the sucrose bulking process should probably only be used when no other processes are available, because of the problems in its resultant products.

Detriments of sucrose bulking

The primary detriment to sucrose bulking is that it yields an artifact that is fairly rigid. For wood, the material in which sucrose has been previously used, this is acceptable and even desirable; wood may reasonably be rigid as part of its diagnostic characteristics. However, it is obviously more desirable is leather can maintain some of its characteristic flexibility. This turns into a judgment call for the conservator; an artifact that is intended

to be simply displayed or one that is rigid to start with, such as sole leather on shoes or the leather used in gaskets or other tools can afford to be still rigid even after treatment is complete. Clothing leather or glove leather, on the other hand, should most likely be approached with an attitude and a process which will allow it to retain its flexibility and drape. Additionally, the initial state of the artifact must be considered. In some cases—such as when an artifact is totally rigid due to total desiccation or impregnation with corrosion products, the flexibility of the product even at the beginning of the treatment is at such a negligible level that it unlikely to be vastly worsened by applying a treatment that generally yields a stiff result.

In the final analysis, I believe that sucrose treatment for leather should be reserved for artifacts that are unable to be stored in a safe environment until the time of their conservation. In this way, sucrose treatment can act as a stopgap: a temporary and reversible treatment that will help to preserve an artifact until it can be more appropriately conserved at a later date. The reversible nature of the sucrose treatment makes this a favorable course of action, however, the fact that artifacts probably undergo some irreversible damage due to the formation of crystals in the fiber matrix makes this a treatment that should be reserved for the instances in which it will cause less harm than will leaving artifacts alone in storage. I recommend the continued use of Passivation Polymer technology when a superior product is required of a conservation strategy.

REFERENCES

Cameron, Esther, James Spriggs, and Barbara Wills
2006 The Conservation of Archaeological Leather. In *Conservation of Leather and Related Materials,* Marion Kite and Roy Thomson, editors, pp. 244-263. Elsevier, Oxford, UK.

Ciliberto, Enrico
2000 Analytical Methods in Art and Archaeology. In *Modern Analytical Methods in Art and Archaeology*, Enrico Ciliberto and Giuseppe Spoto, editors, pp.1-10. J. Wiley and Sons, New York, NY.

Florian, Mary-Lou E.
2006 The Mechanisms of Deterioration in Leather. In *Conservation of Leather and Related Materials,* Marion Kite and Roy Thomson, editors, pp. 36-57. Elsevier, Oxford, UK.

Haines, Betty Mary
2006 Collagen: The Leathermaking Protein. In *Conservation of Leather and Related Materials,* Marion Kite and Roy Thomson, pp. 4-10. Elsevier, Oxford, UK.

Horie, C. Velson
1990 Deterioration of Skin in Museum Collections. *Polymer Degradation and Stability* 29: 109-133.

Jackman, James (editor)
1982 *Leather Conservation: A Current Survey*. Pisces Press, London.

José-Yacmán, Miguel, and Jorge A. Ascencio
2000 Electron Microscopy and Its Application to the Study of Archaeological Materials and Art Preservation. In *Modern Analytical Methods in Art and Archaeology,* Enrico Ciliberto and Giuseppe Spoto, editors, pp.405-444. J. Wiley and Sons, New York, NY.

Kaye, Barry
1995 Conservation of Waterlogged Wood. *Chemical Society Reviews.* 89(1): 35-43

O' Flaherty, Fred, Robert M. Lollar, and William T. Roddy
1958 *Chemistry and Technology of Leather,* Vol. 1. Reinhold Publishing Corporation. New York, NY.

Parrent, James M.
1982 The Conservation of Waterlogged Wood Using Sucrose. Master's thesis, Department of Anthropology, Texas A&M University, College Station.

Randolph, Jr., Anthony G.
2003 The Analysis and Conservation of the Belle Footwear Assemblage. Master's thesis, Departmant of Anthropology, Texas A&M University, College Station.

Reed, Ronald (editor)
1966 *Science for the Students of Leather Manufacture and Technology*. Pergamon Press, Bristol, UK.

Reed, Ronald
1972 *Ancient Skins, Parchments, and Leathers*. Seminar Press, Leeds, UK.

Schmidt, J. D.
1982 Freeze Drying of Historical/Cultural Properties: Available Process in Restoration and Documentation. *Technology and Conservation* 9(1): 20-26.

Smith, C. Wayne.
2003 *Archaeological Conservation Using Polymers: Practical Applications for Organic Artifact Stabilization.* Texas A&M University Press. College Station.

Strzelczyk, Alicja B., L. Bannach, and A. Kurowska
1997 Biodeterioration of Archaeological Leather. *International Biodeterioration and Biodegradation* 39(4): 301-309.

Thomson, Roy
2006 The Nature and Properties of Leather. In *Conservation of Leather and Related Materials,* Marion Kite and Roy Thomson, editors, pp. 1-3. Elsevier, Oxford, UK.

Van Soest, H. A. B., T. Stambolov, and P. B. Hallebeek
1984 Conservation of Leather. *Studies in Conservation.* 29(1): 21-31.

Watson, Jacqui
2004 The Freeze-Drying of Wet and Waterlogged Materials from Archaeological Excavations. *Physics Education.* 39(2)*:* 171-176.

Wilson, John A., and Henry B. Merrill
1931 *Analysis of Leather and Materials Used in Making It.* McGraw-Hill, New York, NY.

CONTACT INFORMATION

Name:	Laura Gail White
Professional Address:	c/o Dr. Frederick Pearl Department of Maritime Studies Texas A&M University at Galveston Galveston, TX 77553
Email Address:	lauragwhite@hotmail.com
Education:	BS in Marine Sciences, Texas A&M University, December 2008 BA in Maritime Studies, Texas A&M University, December 2008 Undergraduate Research Scholar Texas Institute of Oceanography Undergraduate Research Scholar